

Washington State Department of Ecology

Environmental Assessment Program

Standard Operating Procedures for Sampling of Pesticides in Surface Waters

Version 1.0

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EAP003

Please note that the Washington State Department of Ecology's Standard Operating Procedures (SOPs) are adapted from published methods, or developed by in-house technical and administrative experts. Their primary purpose is for internal Ecology use, although sampling and administrative SOPs may have a wider utility. Our SOPs do not supplant official published methods. Distribution of these SOPs does not constitute an endorsement of a particular procedure or method.

Any reference to specific equipment, manufacturer, or supplies is for descriptive purposes only and does not constitute an endorsement of a particular product or service by the author or by the Department of Ecology.

Although Ecology follows the SOP in most instances, there may be instances in which Ecology uses an alternative methodology, procedure, or process.

SOP Revision History

[illegible]

Environmental Assessment Program

Standard Operating Procedure for

1.0 Purpose and Scope

- 1.1 This document is the Environmental Assessment Program (EAP) Standard Operating Procedure (SOP) for collecting samples to monitor pesticides in surface waters.
- 1.2 Monitoring pesticides in surface waters can and often does cover a wide range of objectives. Some studies are designed to look for a few specific chemicals and others are designed to look for a wide range of compounds. The term pesticide is used as a general term to group together many different use classes (herbicides, insecticides, and fungicides) of chemicals. For hydrophobic compounds a relationship between Total Suspended Solids (TSS) and pesticides may exist. This leads many monitoring projects to collect TSS samples alongside pesticide samples.

2.0 Applicability

- 2.1 This procedure is being used in the Washington State Department of Ecology Surface Water Pesticide Sampling Project. It is recommended that this procedure be followed by the Environmental Assessment Program when sampling surface waters to determine the presence and concentration of pesticides.

3.0 Definitions

- 3.1 Certificate of Analysis: Certificate provided by manufacturer ensuring bottles have been cleaned to EPA specifications.
- 3.2 EPA – Environmental Protection Agency
- 3.3 FISP – Federal Interagency Sedimentation Project
- 3.4 MSDS – Material Safety Data Sheet: These data sheets provide important information about a chemical's properties along with health and safety data. Other information about the chemical manufacturer, fire-fighting procedures, protective equipment requirements, and spill clean up procedures are also provided.
- 3.5 MS/MSD – Matrix Spike/Matrix Spike Duplicate
- 3.6 MEL – Manchester Environmental Laboratory: Ecology laboratory that analyzes all pesticide samples.
- 3.7 TSS – Total Suspended Solids: A measure of the total amount of suspended material found in the water column.
- 3.8 US DH-81: depth integrating sampler designed by the USGS for use in wadeable rivers and streams between 1 and 4 feet.
- 3.9 US DH-76: depth integrating hand line sampler designed by the USGS for use in waters that are unsafe to wade but are not deeper than 15 feet.
- 3.10 US D-77: Teflon nozzle and cap for the US DH-81
- 3.11 USGS – United States Geological Survey

4.0 Personnel Qualifications/Responsibilities

- 4.1 1-liter manufacturer cleaned clear glass jars that are organic free with Teflon lid liners and a Certificate of Analysis

5.0 Equipment, Reagents, and Supplies

- 5.1 1-liter manufacturer cleaned clear glass jars that are organic free with Teflon lid liners and a Certificate of Analysis
- 5.2 1-gallon manufacturer cleaned clear glass jars that are organic free with Teflon lid liners and a Certificate of Analysis
- 5.3 125-milliliter manufacturer cleaned clear amber bottles that are organic free with Teflon lid liners and a Certificate of Analysis (preserved by MEL with 1.17 grams of potassium dihydrogen citrate)
- 5.4 Coolers and wet ice
- 5.5 Talc-free Nitrile gloves
- 5.6 Sample tags
- 5.7 Chain of custody seals
- 5.8 TSS bottle (only necessary for studies collecting TSS samples)
- 5.9 US DH-81 (used in waters between 1 and 4 feet but still wadeable) (Figure 1)
- 5.9.1 Wading Rod Handle and extension
- 5.9.2 Teflon US D-77 Caps pre-cleaned¹ to EPA specifications (EPA 1990) and wrapped in aluminum foil with dull side in
- 5.9.3 Teflon US D-77 Nozzles pre-cleaned to EPA specifications (EPA 1990) and wrapped in aluminum foil with dull side in
- 5.9.4 US DH-81A
- 5.9.5 1-liter glass bottles that will fit US D-77 nozzle pre-cleaned to EPA specifications (EPA 1990) with opening covered by dull side of aluminum foil
- 5.10 US DH-76 (used in waters too deep or swift to safely wade but not deeper than 15 feet) (Figure 2)
- 5.10.1 US DH-76
- 5.10.2 Teflon nozzles pre-cleaned to EPA specifications (EPA 1990) and wrapped in aluminum foil with dull side in
- 5.10.3 A length of rope appropriate for the distance to be lowered to and into the water
- 5.10.4 1-liter glass jars that will fit into the sample chamber of the US DH-76 pre-cleaned to EPA specifications (EPA 1990) with opening covered by dull side of aluminum foil
- 5.10.5 Teflon gaskets pre-cleaned to EPA specifications (EPA 1990) and wrapped in aluminum foil with dull side in
- 5.11 Supplies Needed for Cleaning Sampling Equipment
- 5.11.1 Pesticide grade acetone – Acetone is not known to be carcinogenic or teratogenic. The MSDS may be found at <http://www.vwrsp.com/msds/10/BJ0/BJ010-4.pdf>
- 5.11.2 Aluminum foil
- 5.11.3 Liquinox soap

¹ The cleaning procedure for the sampling equipment that needs to be pre-cleaned is provided in Section 6.0.

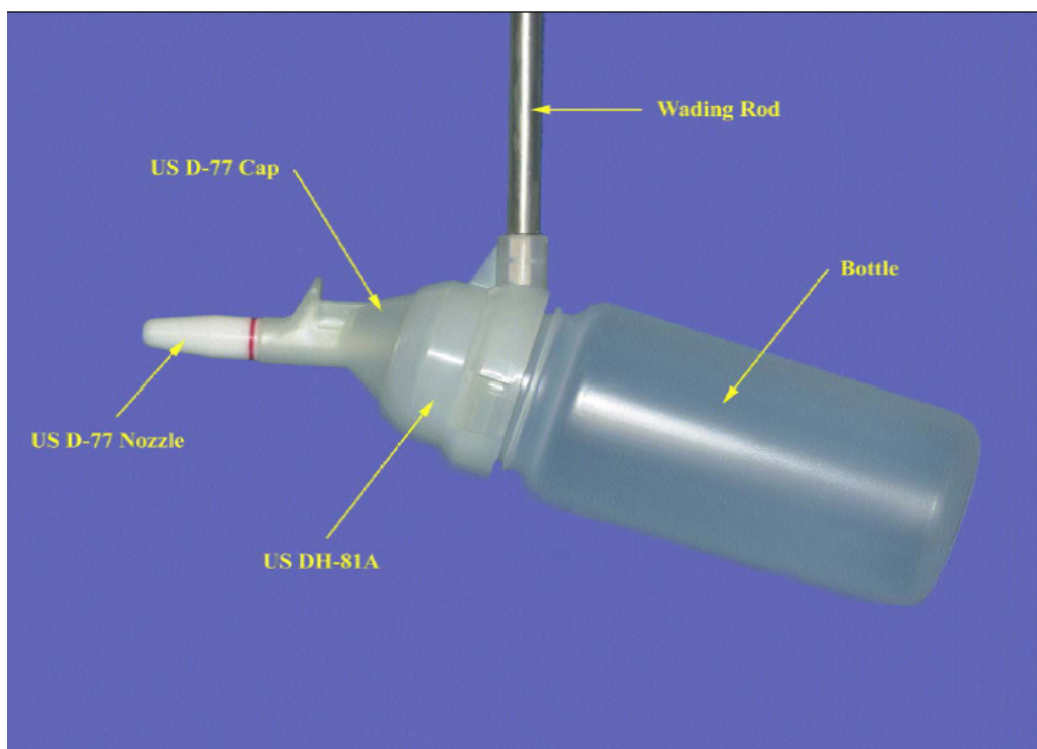


Figure 1. US DH-81 complete assembly.

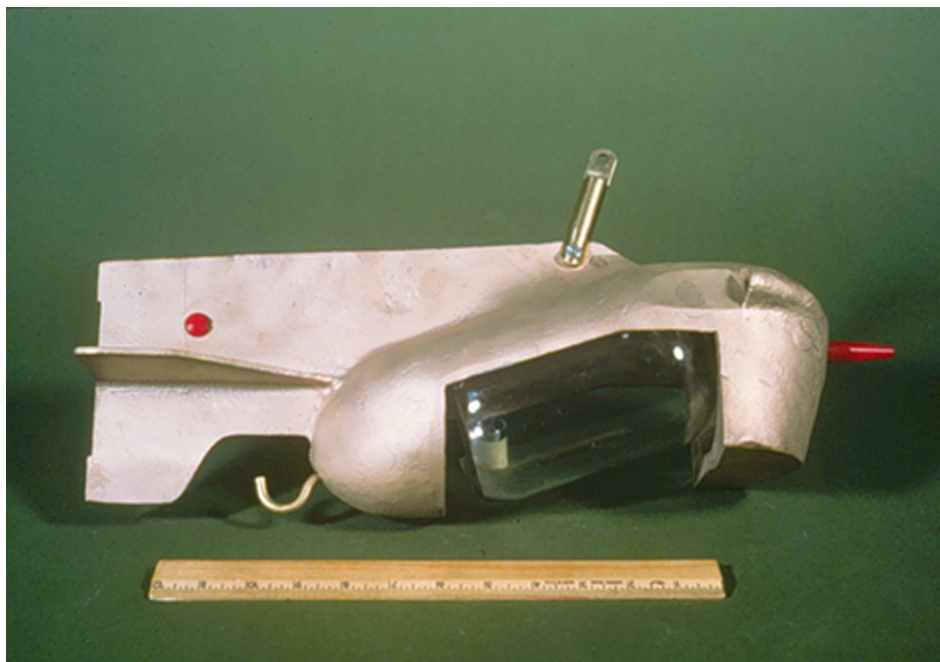


Figure 2. US DH-76 complete assembly.

6.0 Summary of Procedure

6.1 General Sample Collection Techniques

- 6.1.1 Samples will be collected at quarter point transects unless the width of the river or stream makes doing so impractical or useless. A quarter point transect consists of collecting water at 3 points on a line perpendicular to the stream. The points are generally near the right and left bank and near the center of the river or stream.
- 6.1.2 Always collect the sample facing upstream to avoid collecting what is re-suspended by wading. In slow moving waters movement upstream after each transect may be necessary to avoid the plume of re-suspended material.
- 6.1.3 Always wear Nitrile gloves when sampling. The use of the Nitrile gloves protects the sample from contamination from the hands of the sampler.
- 6.1.4 Take care not to bias the sample at any one depth of water. Pesticides may be distributed throughout the water column and by taking a sample at one depth the sampler may miss what is present elsewhere. Particular care should be taken to avoid collecting a disproportionate quantity of water or suspended sediment at the surface of the river or stream. Some pesticides may partition to the surface layer or sorb to bedload constituents. Collecting water in a single region may bias the concentration in the sample.
- 6.1.5 When possible keep the lid on the sample containers between transect points. This will avoid contamination from atmosphere and rain. This is not always possible and should be assessed on a case by case basis.
- 6.1.6 When possible keep the sample containers out of the sun during sample collection. In addition, use amber bottles for those pesticides susceptible to photolysis.
- 6.1.7 Fill sample containers to the shoulder. If testing for highly volatile products, sample containers should be filled to the top of container (no headspace). In this instance, volatile products are compounds with a Henry's Law constant greater than or equal to 10^{-3} atm*m³/mole.
- 6.1.8 Take care not to disturb the substrate with the transfer bottle or collect anything from the substrate.
- 6.2 Handling of Sampling Equipment and Bottles
 - 6.2.1 No part of any piece of sampling equipment that will come into contact with the sample during collection should be touched without wearing Nitrile gloves.
 - 6.2.2 Never touch the inside of a sample container or Teflon lid liner even if wearing Nitrile gloves.

- 6.3 Pre-Cleaning Procedure for US DH-81 and DH-76 parts and bottles, or other pieces of equipment that will come into contact with the sample water
 - 6.3.1 When cleaning sampling equipment follow all safety procedures and wear all necessary safety equipment as detailed in the Ecology Chemical Hygiene Plan.
 - 6.3.2 Wash with hot tap water and brush with Liquinox detergent.
 - 6.3.3 Rinse with tap water 3 times.
 - 6.3.4 Rinse with deionized water 3 times and let drain.
 - 6.3.5 Rinse with pesticide grade acetone and let dry in fume hood.
 - 6.3.6 Wrap in aluminum foil with dull side towards sampling equipment.
- 6.4 Types of Sampling
 - 6.4.1 Grab Sampling – Water collection method using a handheld 1 liter jar in waters less than or equal to 1 foot.
 - 6.4.2 US DH-81 Depth Integrated Sampling – Water collection method using a 1 liter jar attached to a nozzle that is raised and lowered in the water column by a metal handle. This method is used in waters greater than 1 foot but less than 4 feet in depth.
 - 6.4.3 US DH-76 Depth Integrated Hand Line Sampling – Water collection method using a 1 liter jar placed in the housing of a weighted sampling devices lowered by a rope or cable. The US DH-76 method is used in waters greater than or equal to 4 feet but not greater than 15 feet in depth.
 - 6.4.4 Automatic Sampling – water collection method where an automated mechanical sampling device is used to collect water over a period of time or a time specified by the user. This is a specialized type of sampling and will not be covered in this procedures manual.
- 6.5 Grab Sampling
 - 6.5.1 The sampler fills out a field sheet with the date, time, samplers, station name, method of collection, sample number, and weather observations. At this time the sampler will also fill out the sample label with all necessary information. This part of the procedure may be done in the office prior to sampling with the exception of the noting sample time and collection method.

- 6.5.2 The sampler will need 2 1-gallon jars, 1 125-milliliter amber bottle, 1 1-liter transfer jar and 1 1-liter polypropylene bottle (optional). One gallon will be used for the herbicide analysis and the other will be used for the remainder of the pesticide analysis except for carbamates. The 125-milliliter bottle will be used for carbamate analysis. The 1-liter polypropylene bottle will be used for TSS.
- 6.5.3 The sampler will then take all of the containers and sample equipment to the sample site and put on Nitrile gloves.
- 6.5.4 The sampler removes the lid from the transfer jar.
- 6.5.5 The sampler then uses the 1 liter transfer jar to collect water at each point of the transect. The 1-gallon jars will be filled by composting 1 full transfer jar from each point of the transect. This equates to filling the 1-gallon jar 1/3 full at each point on the transect. In most cases a small amount more from each point will be needed to fill the jar to the shoulder. The 125-milliliter bottle and the 1-liter polypropylene bottle will be filled 1/3 full from each transect point.
- 6.5.6 After each sample container has been filled the sampler will place a sample tag with the date, time, study name, station name, laboratory sample number, and type of analysis filled out. Take care to make sure the proper tags are placed on the correct sample containers.
- 6.5.7 Once the sample containers are labeled the samples must be put in ice in a cooler. Placing the samples in a cooler in ice will bring down the temperature and preserve the samples before they are extracted and analyzed.
- 6.5.8 Upon return to the point of departure the sampler will need to fill out a laboratory analysis required sheet and place chain of custody seals on the cooler(s). Laboratory analysis sheets and chain of custody seals may be found at the Operations Center or may be obtained from MEL.
- 6.6 Sampling Using the US DH-81 Depth-Integrating Sampler
- 6.6.1 The sampler will follow most of the directions listed above in the grab sampling section. What is described here pertains mainly to the set-up and use of the US DH-81 depth integrating sampler.
- 6.6.2 Before leaving the van screw the DH-81A adaptor to the wading rod. All other parts of the US DH-81 should be left wrapped in foil until reaching the sample location.
- 6.6.3 Follow procedures 6.4.2-6.4.4. Sampling equipment for the US DH-81 are the US D-77 cap and nozzle, US DH-81A, and wading rod.

- 6.6.4 Remove the foil from the US D-77 nozzle and D-77 cap and put them together. Place the single piece into the US DH-81A and turn the piece to lock it in place.
- 6.6.5 Remove the foil from the opening of the 1-liter pre-cleaned sample jar that fits the DH-81 and screw it into the UD D-77 cap. The US DH-81 is now fully assembled.
- 6.6.6 Fill the bottle at each transect point by moving the assembly up and down in the water column. The rate of movement up and down depends on the velocity of the water. If the water moves fast then the rate will be fast. If the water is slow then the rate will be slow. The rate of upward and downward movement determines how much water from each part of the water column enters the bottle. Rate of movement should be consistent in the vertical profile and between transect points at individual sample sites.
- 6.6.7 Once the bottle is full unscrew it and put the water into one of the sample containers. Repeat this process following procedure 6.4.6.
- 6.6.8 Complete sampling following procedures 6.4.7-6.4.9.
- 6.6.9 When sampling at the station is complete, remove the US D-77 cap and nozzle out of the US DH-81A and place it in a bag for cleaning. These pieces are expensive and should be re-used.
- 6.6.10 Further information on the use of the US DH-81 may be found in the Operator's Manual for the US-DH-81 Depth Integrating Suspended-Sediment Sampler, produced by the Federal Interagency Sedimentation Project (FISP).
- 6.7 Sampling Using the US DH-76
 - 6.7.1 The sampler will use most of the procedures described in the grab sampling section. What is described here mainly pertains to the set-up and use of the US DH-76 sampler.
 - 6.7.2 Follow procedures 6.4.2-6.4.4. Sampling equipment for the US DH-76 is the sampler, nozzle, gasket, and rope.
 - 6.7.3 Once at the sample site remove the sampler from the box and attach the hanger. Tie the rope to the hanger using a secure knot. If possible tie the bitter end of the rope to a solid object to prevent loss of the sampler if the rope is dropped.
 - 6.7.4 Remove the nozzle and gasket and place them in the sampler. Remove the foil from the bottle and place it in the sampler.
 - 6.7.5 Lower the sampler to the water at the first transect point. Lower the sampler into the water and almost to the bottom. Move the sampler up and down until the sampler stops bubbling out of the vent hole. Movement should be at a constant rate and the same at each transect point.

- 6.7.6 Raise the sampler quickly and set it up on the fins. Once set on end, remove the bottle and fill the first sample container. Repeat this process following procedure 6.4.6.
- 6.7.7 Complete sampling following procedures 6.4.7-6.4.9.
- 6.7.8 When sampling is complete, remove the nozzle and gasket and put them in a bag for cleaning and re-use. Parts are cleaned and re-used because they are expensive. Remove the hanger and rope from the sampler and put the sampler back in its box.
- 6.7.9 Further information on the use of the US DH-76 may be found in the Instructions for sampling with Depth-Integrating Suspended-Sediment Samplers US DH-59 and DH-76, produced by FISP.

7.0 Records Management

- 7.1 For each site where pesticides samples are collected, the following must be recorded in a field book:
- Station name
 - Date and time of collection
 - Person or persons collecting samples
 - Weather observations
 - Method used for collection
 - Any field notes that may be pertinent to the investigation (e.g., dead fish)
- 7.2 All incoming MEL data should be stored in an organized manner for easy retrieval and review at a later date (e.g., File folders with the week number and date).

8.0 Quality Control and Quality Assurance Section

- 8.1 Field Quality Control Samples
- 8.1.1 Replicate Samples: Replicate samples consisting of two samples collected at the same time or in series should be included at the discretion of the project lead. These samples will estimate the total random variability (precision) of individual results.
- 8.1.2 Matrix Spike/Matrix Spike Duplicate (MS/MSD) samples: MS/MSD samples consisting of 2 extra volumes of water collected at one station should be included at the discretion of the project lead. These samples are used to evaluate the potential for significant bias in the results due to the interference of the water matrix.

8.1.3 Field Blanks (transfer blanks): A transfer blank is prepared by filling a sample container with pure water during routine sample collection to check for possible contamination from the surroundings. The transfer blank will also detect contamination from the containers or from cross-contamination during transportation and storage of the samples. Transfer blank samples should be included at the discretion of the project lead.

8.2 Results Quality Control

8.2.1 After MEL performs the sample analysis and obtains numerical results the analyst and the lab QA/QC officer will review data and write up a case narrative. The results and narrative will be compiled into a report.

8.2.2 After laboratory review the report will be given to the project lead or other designated project personnel. The person receiving the report will review the results and case narrative and look for any errors, omissions, or inconsistencies. It is the responsibility of the reviewer to investigate any issues and notify the project lead.

9.0 Safety

9.1 Field work done in connection with collecting pesticide samples in surface waters should follow the protocols described in the Environmental Assessment Program Safety Manual, paying special attention to those parts devoted to working in rivers and streams and working near traffic and from bridges.

10.0 References

10.1 Ecology. 2006. Environmental Assessment Program Safety Manual. Washington State Department of Ecology. Olympia, WA.

10.2 Ecology. 2006. Chemical Hygiene Plan & Hazardous Materials Management Plan. Washington State Department of Ecology. Olympia, WA.

10.3 EPA. 1990. Specifications and Guidance for Obtaining Contaminant-Free Sample Containers. OSWER Directive #93240.0-05.

10.4 FISP. 2001. Operator's Manual for the US DH-81 Depth-Integrating Suspended-Sediment Sampler. [http://fisp.wes.army.mil/Instructions%20US DH-81 010612.pdf](http://fisp.wes.army.mil/Instructions%20US%20DH-81%20010612.pdf)

10.5 FISP. 1981. Instructions for Sampling with Depth-Integrating Suspended-Sediment Samplers US D-59 and DH-76. <http://fisp.wes.army.mil/Instructions%20US%20DH-59%20&%20US%20DH-76.pdf>